



# Advancing Solid-Solid Interfaces in Li-ion Batteries

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**Project Manager:** Tien Duong (DOE/EERE)

Project ID # BAT310

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# Overview

## Timeline

- Start: 2019
- Finish: 2022
- 15%

## Budget

- Total project funding
  - DOE share: \$ 1555 K
- FY 20: \$ 455 K
- FY 21: \$ 550 K
- FY 22: \$ 550 K

## Barriers

- Barriers addressed
  - Stability
  - Ion transport
  - Efficiency

## Partners

- Interactions/ collaborations
  - Jeff Sakamoto (UM)
  - Paul Nealey (UC)
  - John Mitchell (ANL)



# Solid-solid Interfaces in Li-ion Batteries: Relevance

## General Objectives

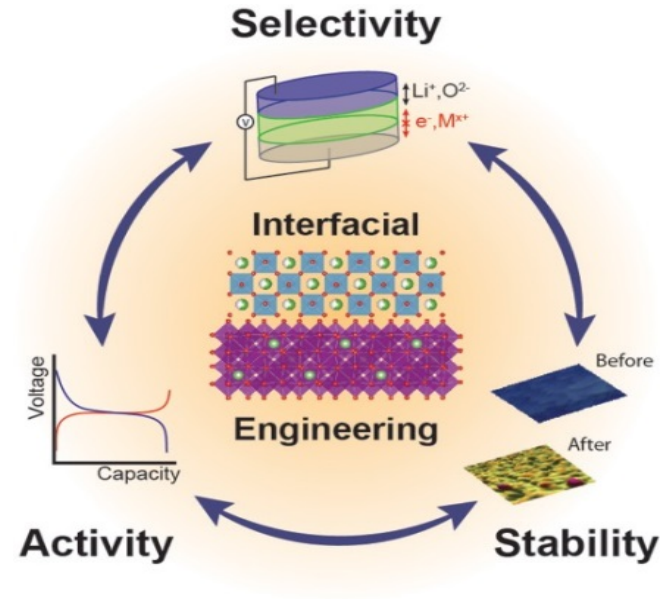
- Develop and use state of the art experimental and computational characterization techniques to establish functional links between activity (cyclability), stability, selectivity, transport and conductivity of electrochemical interfaces and bulk materials in Li-ion battery systems.

## Impact

- Development of stable and effective solid-state electrolyte interface with both metallic Li and the cathode.

## Strategy

- Science-based approach: fast transfer of fundamental knowledge from model to real world systems.

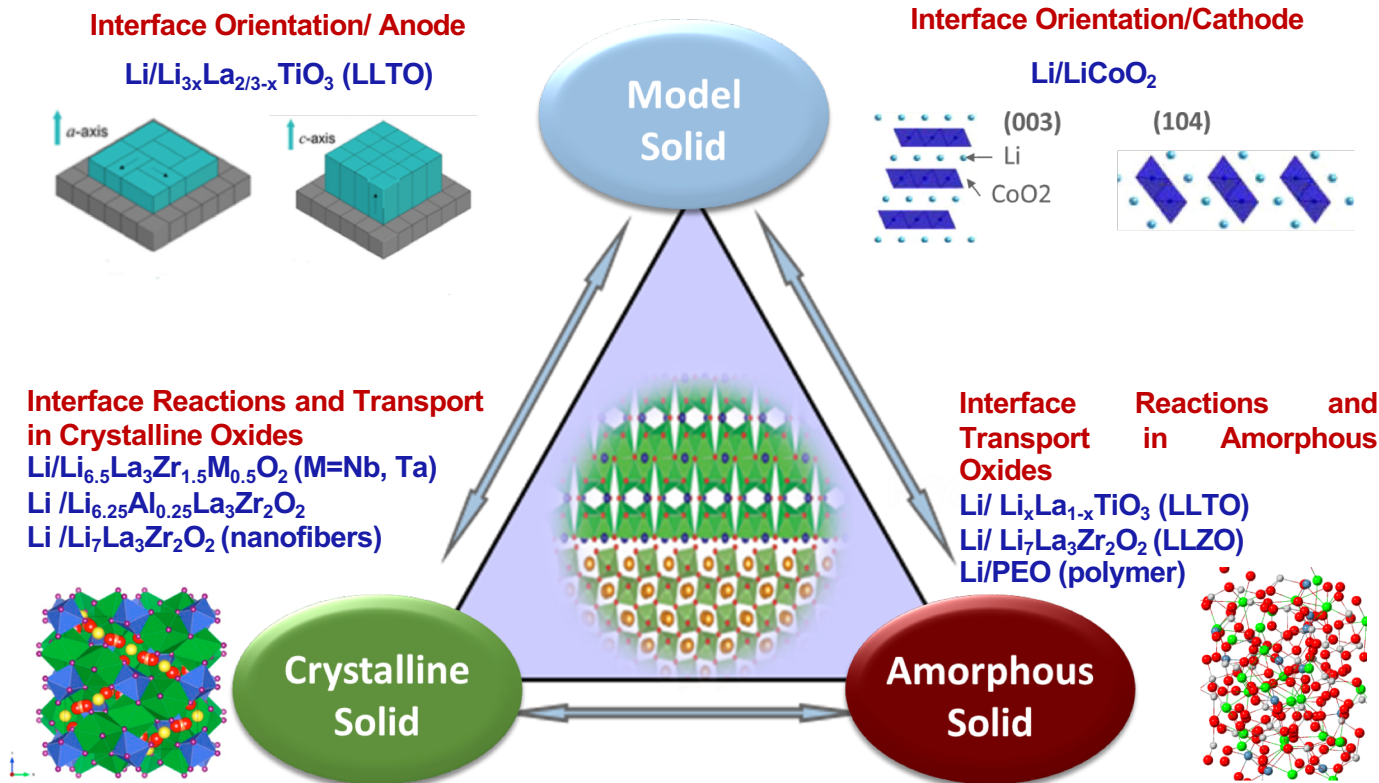


## Milestones

Month /Year	Milestones
Jun/ 19	Distinguish chemical vs. electrochemical reactivity at the interface and bulk of model solid-state electrochemical systems with Li metal anodes and LiCoO <sub>2</sub> cathodes by electrochemical testing and characterization. <i>Completed.</i>
Sep/ 19	Determine dopant-dependent impact on chemical reactivity of different interfaces of solid state electrolytes with lithium metal by computational characterization. <i>Completed.</i>
Dec/ 19	Chemical stability, evaluation, and correlation with interfacial and bulk chemical reactivity for Li/PEO interfaces. <i>Completed.</i>
Mar/ 20	Characterization of Li/LLTO interfaces: effect of crystallinity on surface and bulk reactivity and electrochemical stability. <i>Completed.</i>
Jun/ 20	Characterization of LCO/electrolyte interfaces: effect of crystallinity and orientation on surface and bulk reactivity. <i>In progress.</i>
Sep/ 20	Characterization of lithium interfaces with doped and undoped LLZO, with experimental and modeling study. <i>In progress.</i>



# From Model Systems to Real Solid-Solid: $S_{Li}$ - $S_{EL}$ - $S_{CE}$

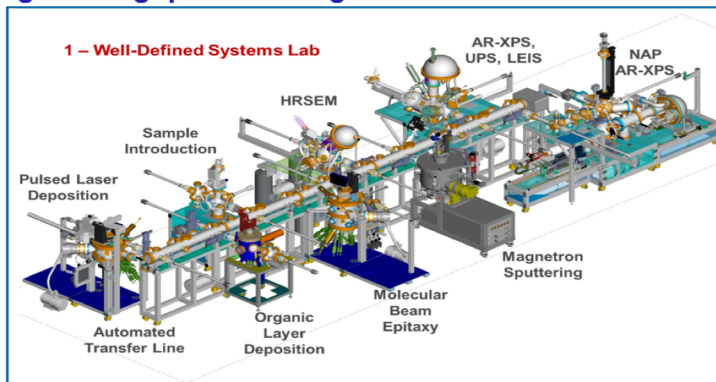


# “Surface Science” Approach

## Deposition Methods

Combination of physical and chemical methods

- ✓ Sputtering
- ✓ Pulse Laser Deposition
- ✓ High throughput modeling
- ✓ Solid Solution
- ✓ Chemical Vapor Deposition
- ✓ Electrochemical

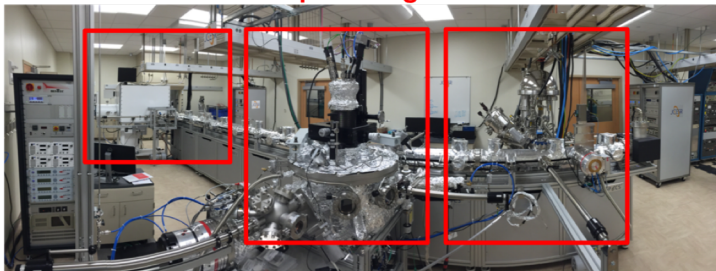


## Characterization Methods

Various ex situ and in situ experimental tools and first principles modeling

- ✓ Low Energy Electron Diffraction
- ✓ X-Ray/Ultraviolet Photoel. Spect.
- ✓ Impedance
- ✓ DFT and Molecular Dynamics
- ✓ Fourier Transform Infrared Spectroscopy
- ✓ Differential Electrochemical Mass Spectrometry
- ✓ Scanning Probe Microscopies
- ✓ Soft X-Ray Spectroscopy

Glove Box    Sputtering    XPS Chamber



XAS,XRD, HAXPES



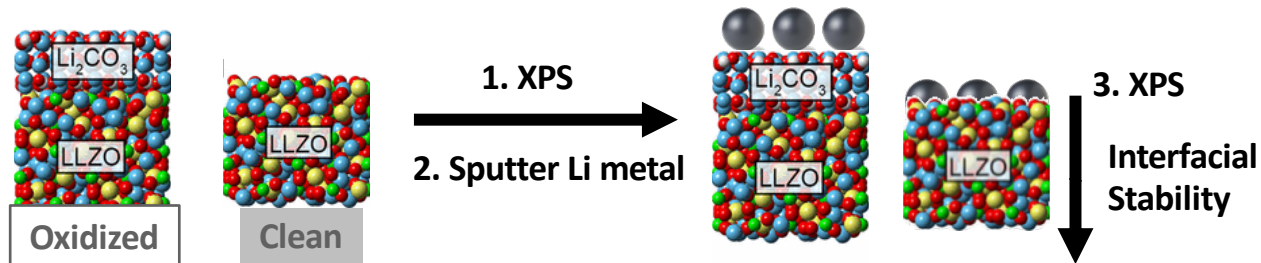
Coin cell assembly



# Major Accomplishments

- Relationship between electrochemical performance of anode-solid electrolyte interface and its structural and chemical properties is established using an Oxygen Deficient Interphase concept.
- Stable and effective solid-state electrolyte interface with metallic Li yields a low charge transfer resistance and enables high critical current densities during cycling. Al-doped LLZO cells were cycled at current densities as high as  $4 \text{ mA cm}^{-2}$  without failure for >300 cycles which is one of the highest current densities for a planar LLZO membrane reported to date.
- Crystallographic orientations of LLTO with more Li intercalation pathways are kinetically more unstable to Li, but long-term reactivity with abundant Li is orientation-independent.
- Amorphous LLTO thin films are stable even after 3 days of contact with excess Li, exhibiting no evidence of surface or bulk reactivity. The Ab Initio Molecular Dynamics results on amorphous LLTO suggest that stability of LLTO films towards Li metal correlates with feasibility of Li ion exchange in LLTO.
- Li metal reacts with PEO, and reactivity increases with heating to  $120^\circ\text{C}$ , which is the main reason for the conductivity increase of PEO (in the range of  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-5} \text{ S/cm}$ ). DFT shows the resulting Li-O bond is ionic ( $\text{Li}^+\text{-O}^-$ ) and can account for the observed ionic conductivity.
- We are able to create epitaxial LCO cathode thin films on top of epitaxial LLTO electrolyte thin films to study reactivity with well-defined cathode/electrolyte systems.

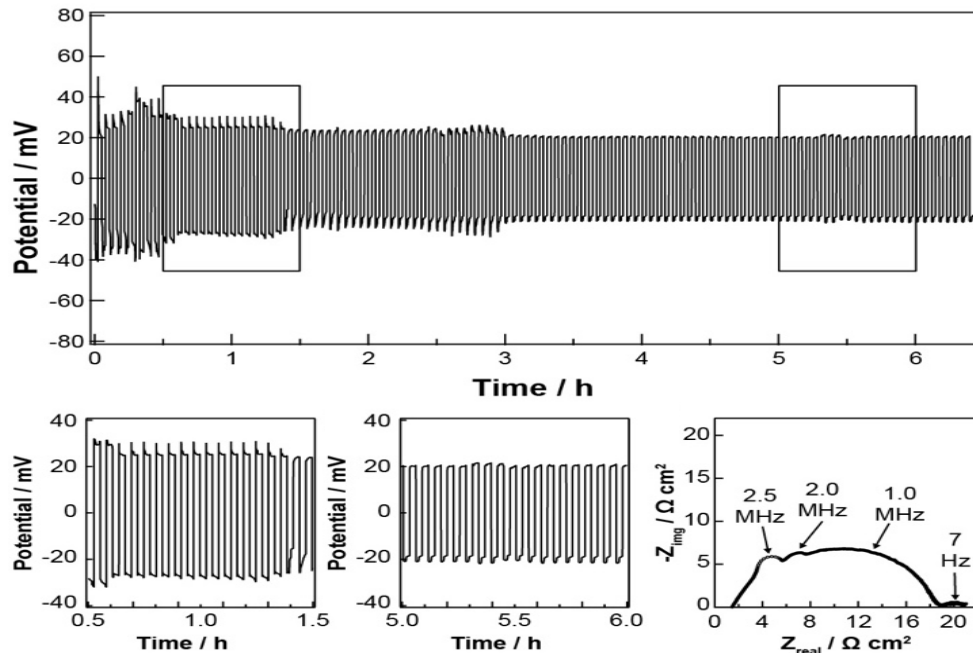
## Previous Work: Doped LLZO/Li Interface Stability



Samples		La	Zr	Dopant
Unstable	Nb-doped $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Nb}_{0.5}\text{O}_{12}$	-	-	-
		-	7.5% $\text{Zr}^{2+}$	15.9% $\text{Nb}^{4+}$
		-		9.0% $\text{Nb}^{3+}$
		-		13.2% $\text{Nb}^{2+}$
Stable	Ta-doped $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$	-	-	-
		-	2.4% $\text{Zr}^{2+}$	-
Stable	Al-doped $\text{Li}_{6.25}\text{La}_3\text{Zr}_2\text{Al}_{0.25}\text{O}_{12}$	-	-	-
		-	9.3% $\text{Zr}^{2+}$ 2.8% $\text{Zr}^0$	-

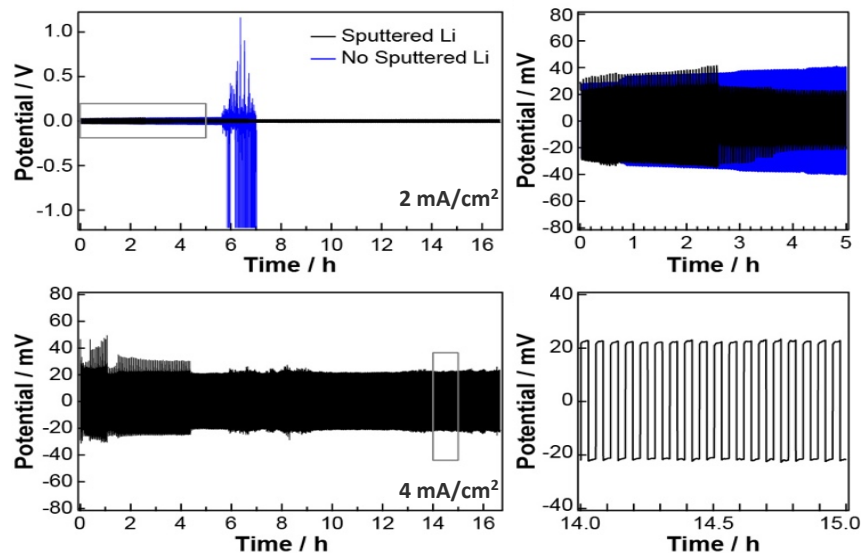
- Stability is determined by surface reactivity with deposited Li metal.

# Li/Ta-Doped LLZO/Li Stability: Electrochemical Stability



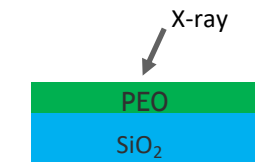
- 100 cycles at  $2 \text{ mA/cm}^2$ , Ohmic behavior for Ta-doped samples, based on the charge transfer resistance
- **Ta-doped LLZO is stable against Li during high current density cycling.**

# Li/Al-Doped LLZO/Li Stability: Electrochemical Reactivity

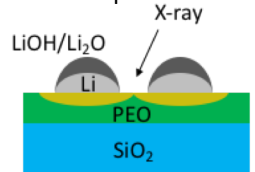


- LLZO cleaning procedure followed with pressed Li foil (without sputtered Li film), improves cycling performance but fails sooner than with sputtered Li film
- Charge and discharge voltage profiles for galvanostatic cycling at  $4 \text{ mA/cm}^2$  follow Ohmic behavior with  $0.5 \text{ } \mu\text{m}$  Li plated/cycle.
- **Symmetric Li/Al-doped LLZO/Li cells able to be cycled at  $2 \text{ mA/cm}^2$  and  $4 \text{ mA/cm}^2$  for  $\geq 300$  cycles.**

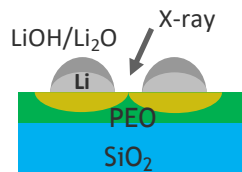
# XPS Study of Li/PEO Interfacial Reactivity



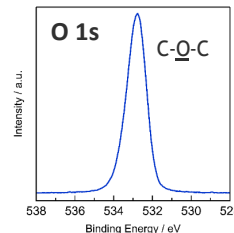
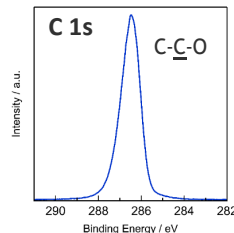
Before Li deposition



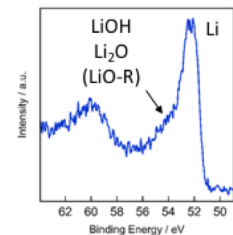
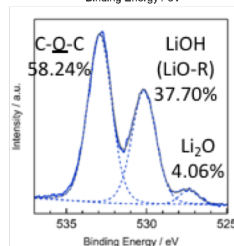
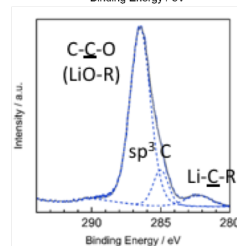
After 20nm Li deposition



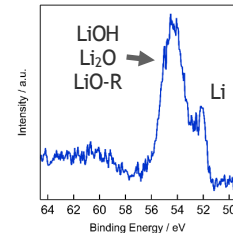
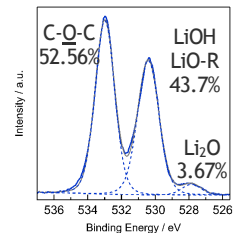
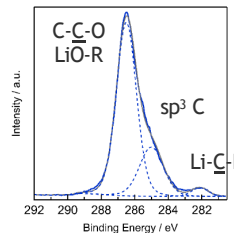
After 20nm Li deposition and 3h of heating



- Spin coat polyethylene oxide (PEO) on clean SiO<sub>2</sub>
- Film thickness ~150 nm
- Measure XPS
- E-beam deposit 20 nm Li
- Measure XPS
- Heat to 120°C for 3h
- Measure XPS

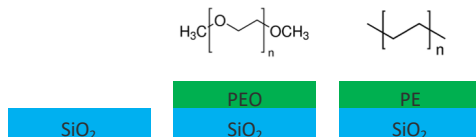


Li 1s

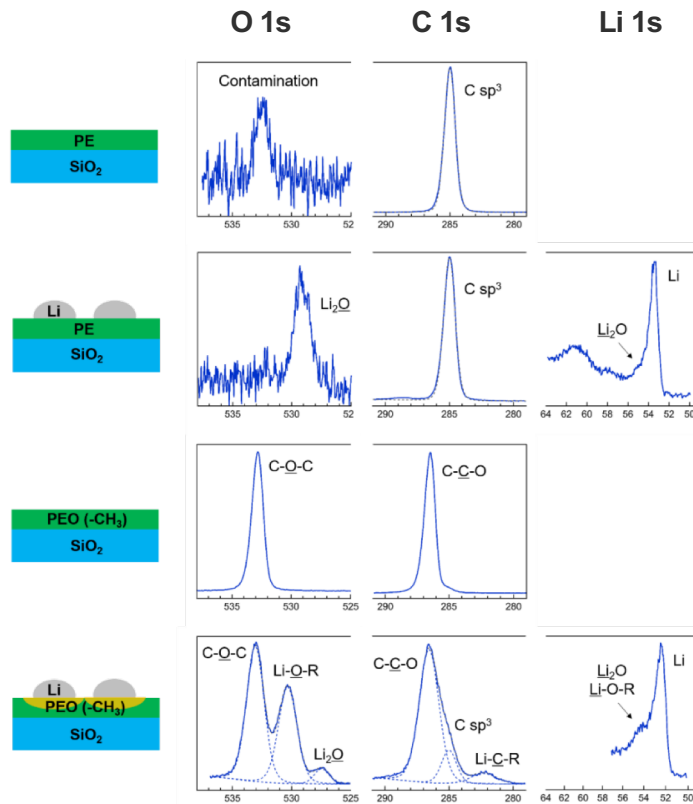


- Li metal reacts with PEO, and reactivity increases with heating to 120°C.

# Comparison of Li/PE vs. Li/PEO Interfacial Reactivity



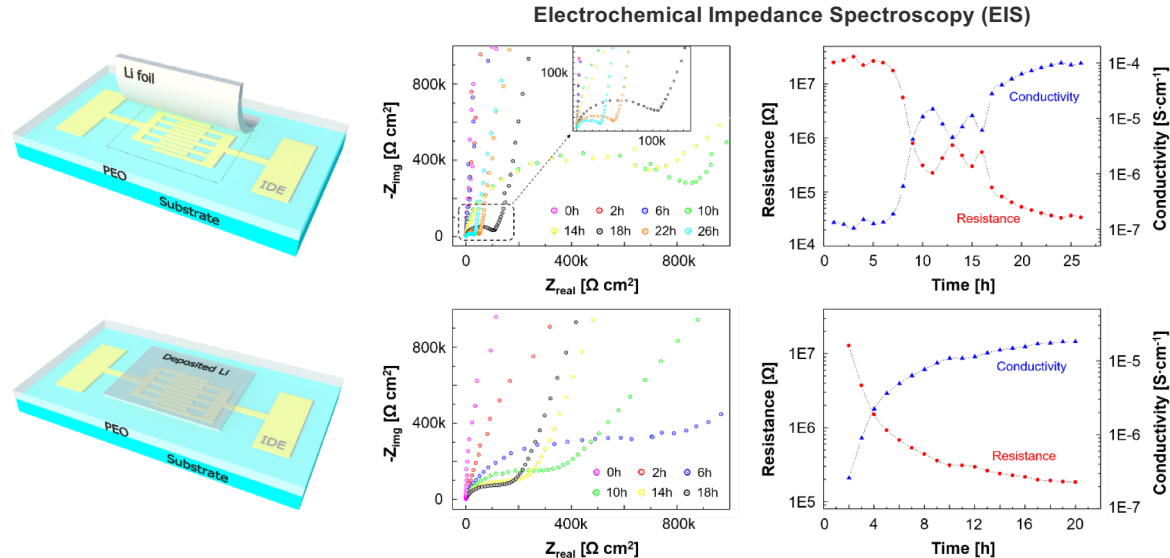
- Polyethylene (PE) does not react with Li metal, PEO reacts with Li metal
- The difference between PE and PEO is the presence of an ether bond in PEO
- **Ether is the only bond that reacts with Li (C-C, C-H do not react).**





# Correlation of Li Reactivity with Ionic Conductivity of PEO

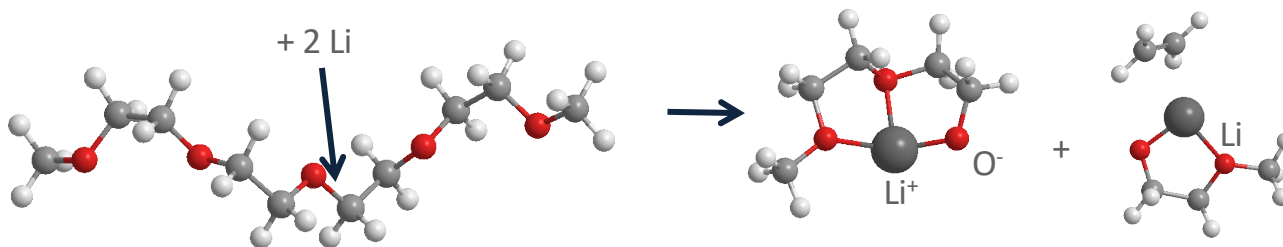
- Prepare interdigitated electrodes (IDE) on SiO<sub>2</sub> substrate
- Spin coat PEO (20k; 20 mg/mL) on IDE, film thickness ~150nm
- EIS measured at 120°C
- Cool the sample down to RT
- Clean Li foil or vacuum deposited Li film, on top of IDEs
- EIS measured at 120°C every hour



- **Li ion reactivity is the main reason for the conductivity increase of PEO (in the range of  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-5} \text{ S/cm}$ ).**
- IDE platform is capable of studying stability of other polymer/Li interfaces.

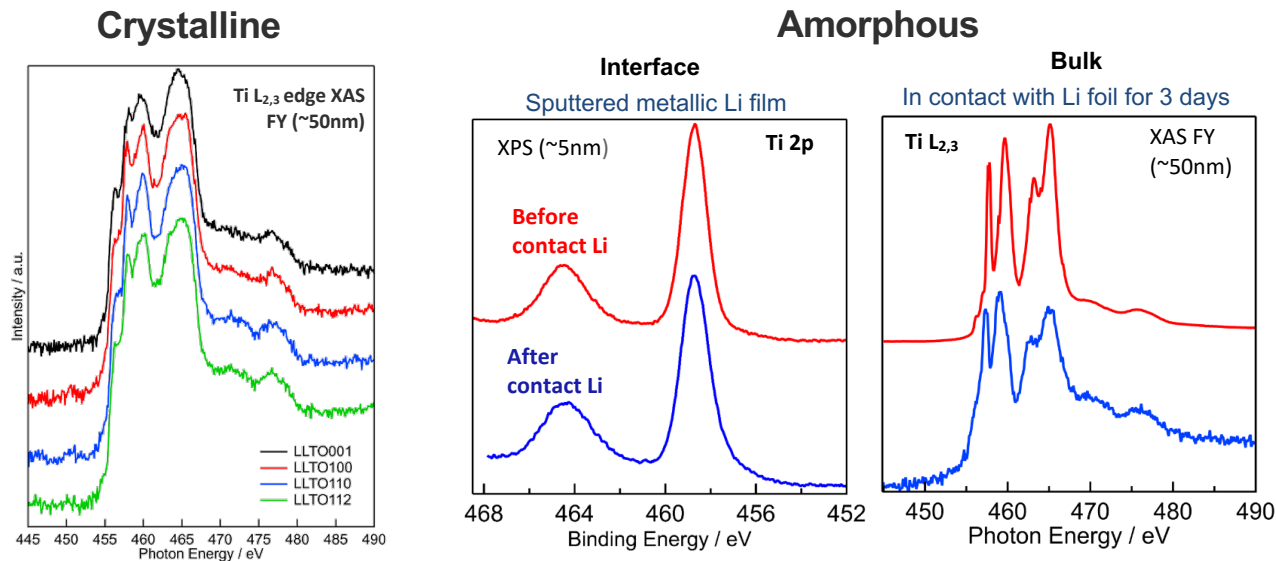
## Modeling of Reactions at a Li/PEO Interface

- Reactions of Li atoms with PEO were examined
  - The Li atoms were assumed to come from the Li surface either by dissolution or by a surface reaction
- DFT was used to calculate the free energies for Li reactions with O-H, C-H, C-O and C-C
  - The most favorable reaction is breaking of a C-O bond



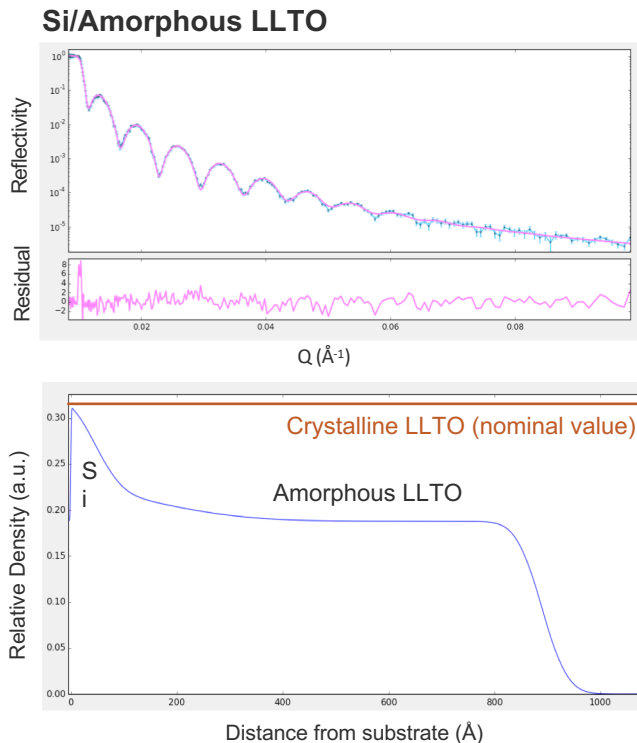
- **The resulting Li-O bond is ionic ( $\text{Li}^+-\text{O}^-$ ) and can account for the observed ionic conductivity.**

# Previous Work: Impact of Orientation and Crystallinity on Reactivity of $\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3$ (LLTO) with Li



- 100-200 nm thick films, crystalline and amorphous, in contact with Li foil for 3 days
- **Long-term bulk behavior of crystalline LLTO with abundant Li source is orientation-independent.**
- **Amorphous LLTO film found to be stable in contact with Li in contrast to crystalline.**

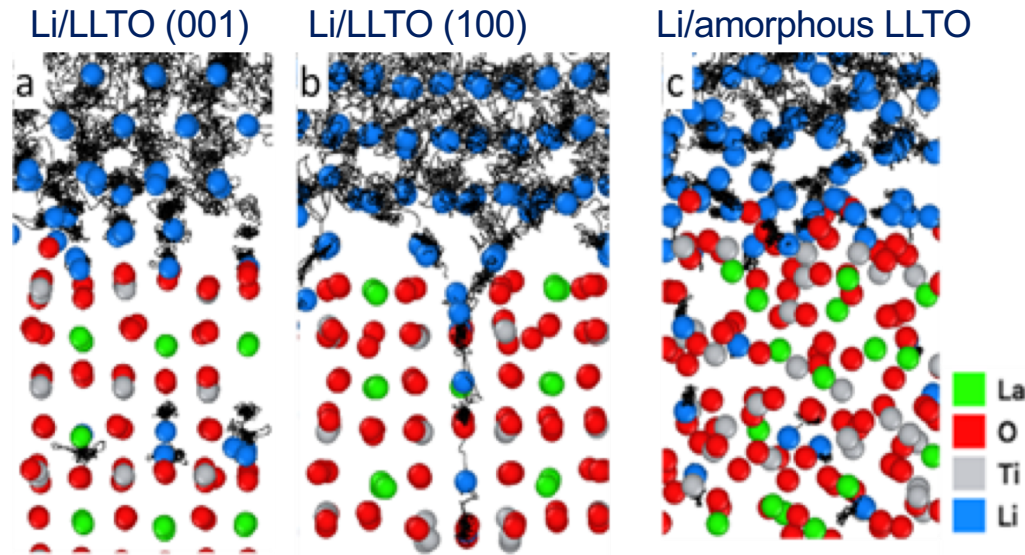
# Characterization of Amorphous LLTO Thin Film Quality via Neutron Reflectivity



- Neutron reflectivity yields baseline measurement of thin film roughness, density and uniformity
- Deposited thin films are smooth with average roughness of  $\sim 4$  nm
- Amorphous LLTO films are significantly less dense on average than crystalline LLTO ( $\sim 70\%$  nominal density)
- Amorphous LLTO films are highly uniform throughout their thickness with no surface layer formation

■ **Amorphous thin films are of high quality for studies of interfacial transport.**

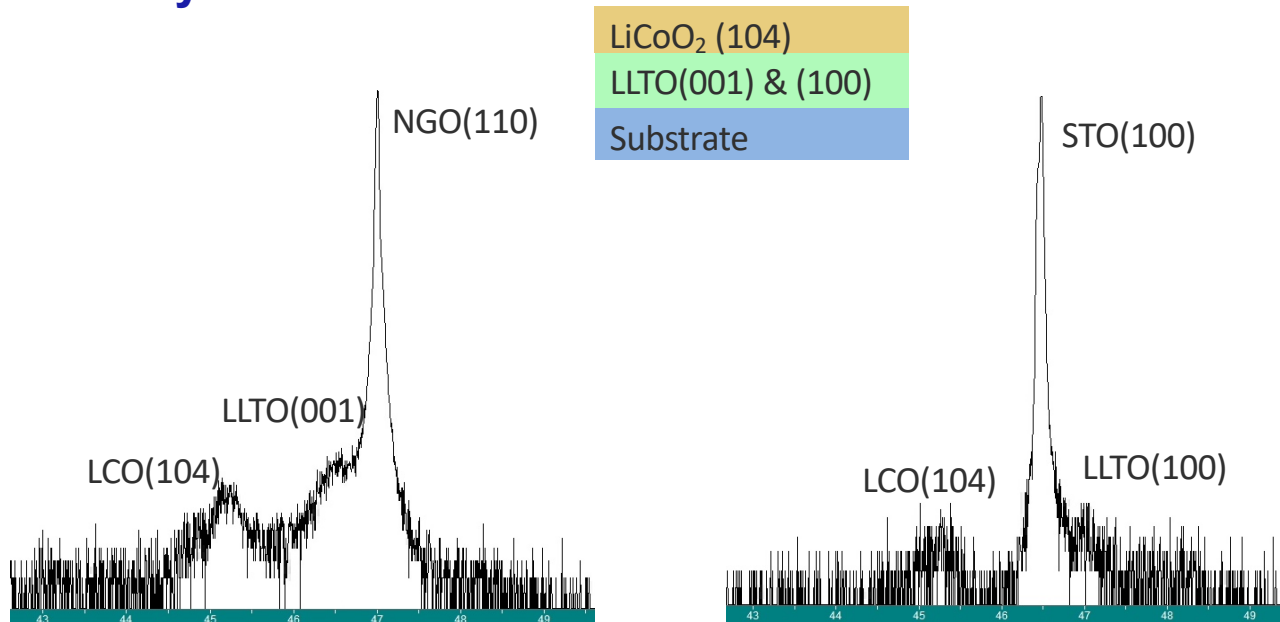
# Ab Initio Molecular Dynamics (AIMD) of Li/LLTO Interface



AIMD trajectories: Li ion trajectories are shown with black lines.

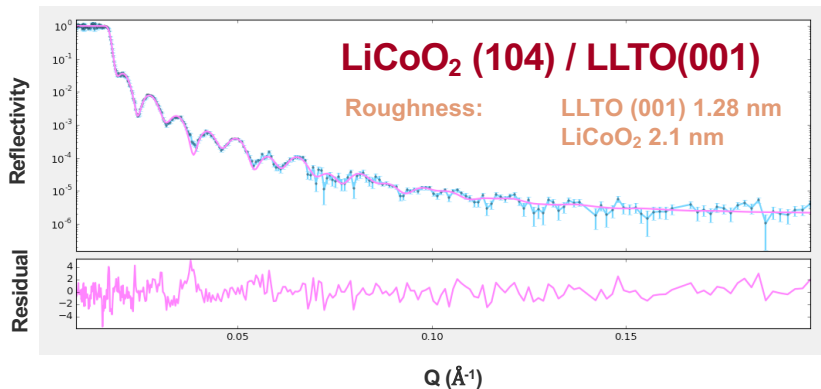
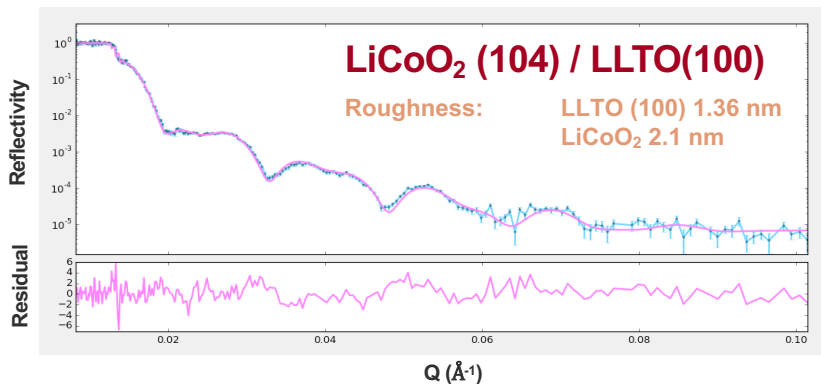
- Li/(001) LLTO interface: no Li exchange between Li metal and LLTO
- Li/(100) LLTO interface: considerable Li exchange between Li metal and Li in LLTO
- Li/amorphous LLTO interface: Li motion was localized within LLTO
- **AIMD simulations suggest that reactivity of LLTO films towards Li metal correlates with feasibility of Li ion exchange in LLTO.**

# In Progress: Cathode Model System: $\text{LiCoO}_2$ /LLTO Interface Stability with XRD



- To improve contact between solid electrolyte and cathode material,  $\text{LiCoO}_2$  cathode was deposited/sputtered onto LLTO at high temperature ( $>600^\circ\text{C}$ )
- **We are able to create epitaxial LCO cathode film on top of epitaxial LLTO electrolyte film to study well-defined cathode/electrolyte system.**

# In Progress: Characterization of Amorphous $\text{LiCoO}_2$ /LLTO Thin Film Interface Quality via Neutron Reflectivity



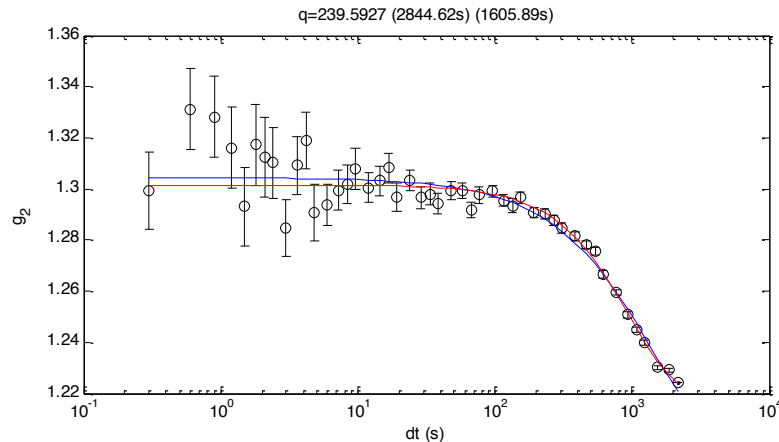
- Neutron reflectivity characterizes interfacial roughness of  $\text{LiCoO}_2$  deposited onto different LLTO orientations at 800°C

- LCO/LLTO interfaces are smooth and of high quality for studies of interfacial reactivity.**

# In Progress: $\text{LiCoO}_2$ /LLTO Interfacial Stability by XPCS of Li-Ion Diffusivity

LLTO(amorphous) 8.14nm
LCO(amorphous) 10nm
LLTO(amorphous) 8.14nm
LCO(amorphous) 10nm
LLTO(amorphous) 8.14nm
LCO(amorphous) 10nm
LLTO(amorphous) 8.14nm
LCO(amorphous) 10nm
Si (100)

Multilayer XPCS (A004-31°C)



- Multilayer grown by pulsed laser deposition (PLD)
- X-ray photon correlation spectroscopy (XPCS) is used to investigate the dynamics of Li fluctuations across the  $\text{LiCoO}_2$ /LLTO interface
- **Allows determination of the activation energy for Li to move across the interface.**



## Remaining Barriers and Challenges

- Control of electrochemical behavior of Li metal anode in a full cell with a solid electrolyte and cathode.
- Control of interface properties on the cathode side to enable battery cell configurations.
- Mechanistic understanding of differences between amorphous and crystalline electrolyte behavior and their impact on electrochemical cycling.



# Proposed Future Work

## ***FY2020 Li-Solid Electrolyte systems:***

- Characterization of LCO/electrolyte interface: understanding the effect of crystallinity and orientation on surface and bulk reactivity.
- Characterization of lithium interfaces with doped and undoped LLZO, with experimental and modeling study.
- Perform DFT calculations to understand reactivity of different interfaces of solid state electrolytes with lithium metal.

## ***FY2021 Toward full cells with Li metal anode:***

- Understanding origins of interfacial resistance at solid electrolyte/cathode.
- Stability of interfaces in Li/SSE/cathode using experiment and theory.

Any proposed future work is subject to change based on funding levels.

## Response to last year reviewer's comments

**Comment:** The reviewer stated that the work largely used Li-Li cells and the specification of the electrolyte layer is not provided (thickness and density or residual porosity).

**Response:** The crystalline LLTO layers (grown by PLD) are single crystal (having bulk density and zero porosity). The thickness is roughly 200 nm. Density of the amorphous LLTO films is lower than crystalline (~70%) but exhibit no porosity. Underlying mechanisms that induce failure at the Li interface with LLZO or LLTO are not well understood and studying thin films enables us to eliminate effects of porosity and impurities in order to isolate the effect of key parameters such as orientation, crystallinity or dopants.

**Comment:** The reviewer suggested that the researchers work as a team to help develop a more robust mechanism for their oxygen-deficient layer as it would be interesting to locally provide more oxygen on the surface to investigate how that changes the performance.

**Response:** We appreciate the suggestion and will continue to develop the mechanism for the oxygen deficient layer. We will study both computationally and experimentally how the changes in oxygen concentration change the performance. Also, we will develop different Li deposition techniques to vary both oxygen composition and deposition energy to optimize the oxygen deficient interphase.



## Response to last year reviewer's comments

**Comment:** The reviewer observed the need for studying the mechanical behavior. It was unclear to the reviewer from the slides under “In progress” how the team will measure the electrochemical and mechanical behavior of model systems such as thin films of lithium cobalt oxide ( $\text{LiCoO}_2$ ) (104)/LLTO (001) & (100)/Substrate, since these structures cannot readily be used for these measurements.

**Response:** The purpose of these model systems is to study the migration of Li ions across the interface and determine whether there exists a difference due to the orientation of LLTO, which can yield anisotropic behavior (as shown on slide 15 for the case of Li/LLTO). The substrates are primarily used to epitaxially grow LLTO films of different crystal orientations. The model systems are currently designed for studies of other properties such as crystal orientation dependence and interfacial mobilities. Studies of interfacial mechanical properties are certainly of interest but are beyond the scope of this project.



## Collaborations with other Institutions and Companies

- Jeff Sakamoto (UM)
  - ✓ Anode/Electrolyte interfaces, Li/LLZO
- Paul Nealey (Argonne MSD)
  - ✓ Synthesis and Characterization of Amorphous Materials
- John Mitchell (Argonne MSD)
  - ✓ Synthesis and Characterization of Complex Oxide Materials



# Selected Publications and Invited Presentations

## Publications:

1. **Interface Design for High Current Density Cycling of Solid State Battery** Tepavcevic, S., Connell, J. G., Zhu, Y., Zapol, P., L. A., Freeland, J. W., Fong, D. D., Stamenkovic V., Markovic, N. M. (submitted to EES)
2. **Comparison of chemical reactivity of amorphous LLTO to epitaxial films of different orientation towards metallic Li anode**, Zhu, Y., Zapol P., Tepavcevic, S., Connell, J. G., Freeland, J. W., Fong, D. D., Curtiss, L. A., Markovic, N. M. (in preparation)

## Presentations:

1. Sanja Tepavcevic, Yisi Zhu, Justin G. Connell, Peter Zapol, Jeff Sakamoto, Larry A. Curtiss, Dillon D. Fong, John W. Freeland, Nenad M. Markovic. "Advancing Solid State Interfaces in Li-ion Batteries." Solid State Electrolytes Meeting, October 24, 2019 Richland, WA

## Patents:

1. **IN-19-084 "INTERFACE DESIGN FOR HIGH CURRENT DENSITY CYLING OF SOLID STATE BATTERY"** filed in the U.S. Patent and Trademark Office on February 7, 2020 as Application Serial No. 16/784,54.
2. **IN-19-173 "IMPROVED ION CONDUCTIVITY OF POLYETHYLENE OXIDE BY IN-SITU LITHIUM SALT FORMATION"**

